the final precipitation at —30°C. was diluted with two volumes of water, acidified with HCl, and the fatty acids were extracted. All fatty acid fractions were weighed, and the Hanus iodine value and refractive index were determined. The results are shown in Table II.

Discussion

From a consideration of the data in Table I showing the effect of varying the mole ratio of urea to menhaden-oil fatty acids, it is evident that there is considerable selectivity in the fatty acids precipitated when the moles of urea present are less than the quantity required for maximum precipitation. Thus, at a mole ratio of 4.6, the fatty acids obtained from the precipitates are highly saturated, but at higher mole ratios more unsaturated fatty acids are complexed by urea.

From the analysis of menhaden oil and the results in Table I it would appear that virtually all the saturated and monoenoic fatty acids are precipitated at a mole ratio in the region of 12:1 to 13:1. When the mole ratio is further increased, more of the less stable dienoic fatty acid complexes are precipitated. This observation is in agreement with the results of Redlich and co-workers (7), who observed that substances forming unstable urea complexes were capable of precipitation from mixtures of reactants. Furthermore the data indicate that fatty acids with more than two double bonds are not present in the precipitates in other than minute quantities.

TABLE II

Characteristics of Fractions Obtained from Marine-Oil Fatty Acids by Urea[a] Crystallization at Different Temperatures

Fatty acids	Weight (g.)	Hanus I. V.	Refractive index[b]
From Menhaden Oil			
Total fatty acids	50.0	159.5	1.4705
25°C. fraction	13.9	19.4	1.4431
1°C. fraction	8.7	46.0	1.4548
—18°C. fraction	3.0	82.7	1.4601
—30°C. fraction	0.1	......	1.4901
Unprecipitated fatty acids in filtrate	24.2	255.0	1.4891
From Herring Oil			
Total fatty acids	50.0	136.4	1.4736
25°C. fraction	12.2	47.7	1.4570
1°C. fraction	9.1	55.2	1.4575
—18°C. fraction	4.7	75.8	1.4667
—30°C. fraction	1.9	92.9	1.4687
Unprecipitated fatty acids in filtrate	21.2	246.0	1.4899
From Tuna-Body Oil[c]			
Total fatty acids	50.0	149.6	1.4707
25°C. fraction	6.9	27.7	1.4336
1°C. fraction	9.2	42.4	1.4567
—18°C. fraction	3.9	61.9	1.4594
—30°C. fraction	0.1	......	1.4865
Unprecipitated fatty acids in filtrate	24.8	243.1	1.4867
From Seal Oil[d]			
Total fatty acids	50.0	129.0	1.4784
25°C. fraction	5.4	52.3	1.4584
1°C. fraction	10.1	63.3	1.4592
—18°C. fraction	3.4	75.5	1.4623
—30°C. fraction	2.6	116.5	1.4692
Unprecipitated fatty acids in filtrate	24.7	210.5	1.4775
From Salmon-Egg Oil			
Total fatty acids	50.0	206.8	1.4757
25°C. fraction	10.7	46.7	1.4567
1°C. fraction	9.2	82.9	1.4595
—18°C. fraction	5.0	153.0	1.4711
—30°C. fraction	0.2	......	1.5174
Unprecipitated fatty acids in filtrate	24.5	290.0	1.4953
From Salmon-Head-and-Viscera Oil			
Total fatty acids	50.0	144.6	1.4729
25°C. fraction	6.0	43.7	1.4573
1°C. fraction	12.0	59.5	1.4592
—18°C. fraction	5.5	119.5	1.4599
—30°C. fraction	0.1	......	1.4760
Unprecipitated fatty acids in filtrate	17.1	241.6	1.4867

[a] Fractionations were made in methanol solution at a mole ratio of urea to fatty acids of approximately 9:1.

[b] All refractive index values are calculated to 20°C. by use of the factor —0.000365 per degree.

[c] The sample of tuna-body oil contained a considerable amount of oxidized fatty acids.

[d] The seal-oil fatty acids contained some waxy acidic substance that was only moderately soluble in methanol.

The results of these experiments show that fatty acid fractions of almost any desired iodine value ranging to above 300, a degree of unsaturation corresponding to three to four double bonds per molecule, can be prepared readily from menhaden oil or from other oils of similar characteristics.

The experiments dealing with the effect of temperature on the precipitates bear out the previous results. In addition, from the data in Table II it is evident that menhaden oil has a considerably higher content of saturated fatty acids than any of the other oils used in this work. This fact is borne out by published analyses of the oils.

The fractions precipitated at —18°C. and the very small yields obtained at —30°C. contain appreciable amounts of the dienoic fatty acids whereas the 25°C. and 1°C. fractions contained no measurable quantities of these acids. An especially high proportion of dienoic acids is apparently present in the complexes obtained from the salmon oils.

Summary

In two series of experiments, marine-animal-oil fatty acids were fractionated with urea using methanol as solvent.

In the first series, menhaden-oil fatty acids were fractionated at 1°C. Almost all the saturated and monoenoic fatty acids were removed at mole ratios of 12:1 to 13:1. At higher ratios increasing amounts of the less stable dienoic fatty acids were precipitated. By the use of the appropriate ratio, fractions having iodine values above 300 were prepared.

In the second series, fatty acids from the oils of menhaden, herring, tuna, seal, salmon eggs, and salmon heads and viscera were fractionated at a mole ratio of urea to fatty acid of 9.2:1. At 25° and 1° the complexes were composed almost entirely of saturated and monoenoic fatty acids, but as the temperature was lowered to —30°, the content of dienoic fatty acids in the precipitates increased.

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CORRECTION

From the Netherlands J. P. Spruyt writes that the word squalene which appeared in his paper in the April 1955 issue (vol. 32, pp. 197–200) should have been squalane instead. His correction on the galley proof apparently was overlooked by the printer and editorial staff.